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12C. Non-Linear Chromatography (IUPAC Recommendations 1996)

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Synopsis

This report summarizes and comments on terms and symbols used for the description of non-linear chromatography.

Introduction

In the IUPAC recommendations *Nomenclature for Chromatography* [1], the conditions of linear chromatography are tacitly assumed. In all versions of chromatography, however, non-linear effects are common. These are seen as concentration-dependent retention times and asymmetric (e.g. tailing or fronting) peaks. Asymmetric peaks can result from a number of other causes as well, i.e. large extra-column volumes. In many applications, non-linear effects are disadvantageous as they decrease peak resolution and disturb quantitative evaluation. However, in preparative chromatography, heavy overloading is employed in order to increase material throughput, leading to prominent non-linear effects. A comprehensive text on non-linear chromatography has recently been published [2].

In this paper, some of the concepts and terms used for non-linear chromatography are described. It is to read as a complement to the *Nomenclature for Chromatography* (CN) [1], to which numerous references are given.

1. Terms Related to Isotherms

1.1 Distribution Isotherm (in Chromatography)

The equilibrium relation between the concentration of a sample component in the stationary phase c_S, and in the mobile phase c_M, expressed as a function $c_S = f(c_M)$.

Note: The relation can be influenced also by concentrations of other sample components. c_S and c_M are usually expressed *per unit volume of the phase*; c_S may also be expressed *per mass of the dry solid phase* or *per unit surface area*. This is discussed in CN, section 3.9.

In some versions of chromatography, a distribution isotherm can be seen as a *partition isothem*, an *adsorption isotherm*, or a combination of these, depending on the mechanism of separation (cf. CN 1.5).

1.1.1 Partition isotherm (in chromatography) Isotherm describing partition of the sample component between the bulk of a liquid stationary phase and a liquid, gaseous or supercritical mobile phase.

1.1.2 Adsorption isotherm Isotherm describing adsorption of the sample component on the surface of the stationary phase from the mobile phase.

Note: Adsorption isotherms can be described by Langmuir, Freundlich and other adsorption isotherm equations. See [3], p. 13.

1.2 Linear Distribution Isotherm

A distribution isotherm which can be approximated as $c_S = K_C\, c_M$, where K_C is a constant.

Note: At low concentrations, all distribution isotherms tend towards being linear. K_C is the *distribution constant* (cf. CN 3.9 and 3.4 in ref. 4).

1.3 Non-linear Distribution Isotherm

A distribution isotherm which is not linear.

Note: A non-linear isotherm can have several shapes, as classified by Brunauer *et al.* [5]. In chromatography convex or concave shapes are common, as well as combinations.

1.3.1 Convex isotherm Distribution isotherm, the slope of which is continuously decreasing (see **Figure 1A**).

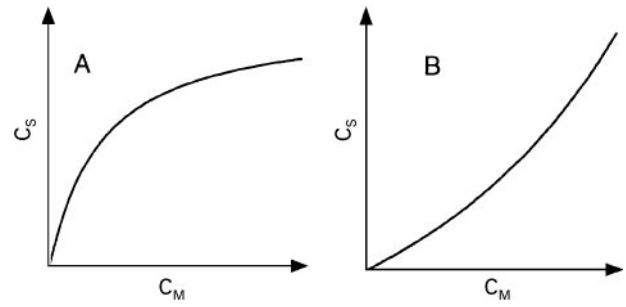

Figure 1 Different types of distribution isotherms for the concentrations of a compound in the stationary (c_S) and mobile (c_M) phases: (A) convex isotherm, (B) concave isotherm.

Note: The resulting chromatographic peak is tailing (CN 3.3.08). Adsorption isotherms are often of this type. A special case is the Langmuir adsorption isotherm.

1.3.2 Concave isotherm Distribution isotherm, the slope of which is continuously increasing (see Figure 1B).

Note: The resulting chromatographic peak is fronting (CN 3.3.09). In gas-liquid chromatography, overloading often results in a concave isotherm.

2. Types of Chromatographic Processes

2.1 Linear Chromatography

Chromatographic process, where the retention is governed by a linear distribution isotherm.

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2.2 Non-linear Chromatography

Chromatographic process, where the retention is governed by a non-linear distribution isotherm.

2.3 Ideal Chromatography

Chromatographic process, where no peak-broadening effects (such as diffusion, slow mass transfer, etc.) operate.

Note: This is a hypothetical case, implying that the plate number (CN 3.10.03) is infinite.

2.4 Non-ideal Chromatography

Chromatographic process with normal peak-broadening effects.

2.5 Non-ideal, Linear Chromatography

Chromatographic process, where the retention is governed by a linear distribution isotherm and normal peak-broadening take place.

Note: This case is commonly assumed in analytical chromatography, as described in ref. 1.

2.6 Ideal, Non-linear Chromatography

Chromatographic process, where only the curvature of the distribution isotherm determines the shape of the peaks while other peak-broadening processes are neglected.

Note: The assumption of ideal, non-linear (INL) chromatography is often made in order to facilitate theoretical treatments. It can be justified in cases of efficient columns and distribution isotherms with prominent non-linearity.

2.7 Non-ideal, Non-linear Chromatography

Chromatographic process, where both isotherm curvature and other peak-broadening processes (such as diffusion) contribute to the peak shape.

Note: This case comprises most peaks in common practice that are characterized as 'tailing' or 'fronting'.

3. Retention Parameters in Non-Linear Chromatography

3.1 Total Retention Volume (Time) in Ideal, Non-linear Chromatography ($V_{R(INL)}$, $t_{R(INL)}$)

The volume of mobile phase entering the column between sample introduction and the emergence of a certain concentration of the sample component at the column outlet; or the corresponding time.

Note: This volume (time) can be measured to the peak maximum or to other points on the peak. Under the conditions of ideal, non-linear chromatography, the total retention volume is given by:

$$V_{R(INL)} = V_M + \frac{\partial c_S}{\partial c_M} \cdot V_S \tag{1}$$

With a constant flow rate F_c through the column, the *total retention time in ideal, non-linear chromatography* is given by $t_{R(INL)} = V_{R(INL)}/F_c$ as in CN 37.05. If appropriate, V_S in equation (1) may be exchanged for the surface area of the stationary phase or the mass of the stationary phase, depending on the definition of c_S (cf. 1.1 and CN 3.9). In the case of a linear distribution isotherm, equation (1) is in agreement with corresponding equation in CN 3.9.01. Note that the retention is determined by the *slope* of the isotherm, not by the *ratio* c_S/c_M. This particular point was discussed by Helfferich [6].

Typical peaks in ideal, non-linear chromatography are shown in **Figure 2**. The curved ('diffuse') flanks are described by equation (1) and the area of the peak (determined by the total amount of the sample component) gives the position of the vertical flank.

The retention volume in ideal, non-linear chromatography is thus a function of the mobile phase concentration of the sample component. The retention volume to the maximum of the peak (cf. CN 3.7.05) is related the value of the slope of the distribution isotherm at the maximum value of the mobile phase concentration of the sample component at the column outlet.

The broadening of the peaks in Figure 2 is totally caused by the isotherm non-linearity. As the derivation of equation (1) implies that the plate number N is infinite, it is obviously meaningless to apply equations such as those described in CN 3.10.03 and 3.10.04 to characterize peaks of this kind.

3.2 Total Retention Volume (Time) in Non-ideal, Non-linear Chromatography ($V_{R(NINL)}$, $t_{R(NINL)}$)

The definition is analogous to that in 3.1 above.

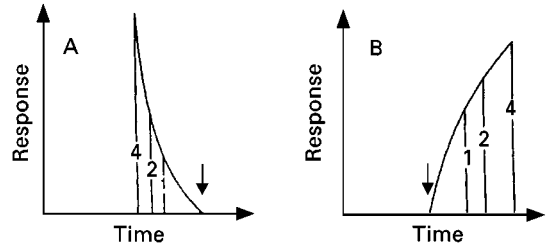

Figure 2 Typical peak shapes in ideal, non-linear chromatography. Peaks A and B are generated by equation (1) from the distribution isotherms in Figures 1A and 1B, respectively. The numbers 1, 2, 4 signify the relative amounts of the sample component. The retention time at low sample concentration, i.e. in the case that the curvature of the distribution isotherm is negligible, is indicated with an arrow.

Note: In the general case of non-ideal, non-linear (NINL) chromatography, only numerical solutions to the applicable non-linear partial differential equations involved can be found. Several examples are found ref 2, where simulated NINL peaks are compared with INL peaks with the same parameters, except for the diffusion term. It is seen that the NINL peaks are lower, wider and more tailing than the INL peak. With a reasonably efficient column ($N > 5000$ for symmetric peaks), the difference might be neglected for practical purposes.

Thus, even if no explicit equation for the retention volume in the NINL case can be given, Equation (1) is approximately valid also for a NINL peak, the discrepancy depending on the column efficiency.

To measure distribution isotherms by chromatography, the so-called *Elution by Characteristic Point* (*ECP*) method has been suggested. Retention volumes to several points on the curved flank of an experimental peak are measured and related to the solute concentration at those points. The distribution isotherm can then be calculated using Equation (1). The validity of the method depends on the efficiency of the column used for these measurements.

There is no known general way of calculating meaningful peak broadening parameters, such as plate numbers from NINL peaks. As the NINL case in practice is common, this observation is important: The usual equations for the calculation of plate numbers (such as those described in CN 3.10.03) should only be applied to effectively symmetrical peaks.

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12D. Supercritical Fluid Chromatography and Extraction (IUPAC Recommendations 1993)

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Abstract

The report present definitions for the terms and symbols used when supercritical fluids are employed as the liquid phase in chromatography and allied areas including sample extraction. The terms supplement those in the general Nomenclature for Chromatography and includes additional more specific terms.

Introduction

Following the General Assembly Meeting in 1989 the Limited Life Time Commission for Chromatography and Other Analytical Separations took over the work on the nomenclature for chromatography that had previously been undertaken by the Commission for Analytical Nomenclature. A major part of the work was the Nomenclature for Chromatography which had been developed over a number of years by L. S. Ettre and has recently been published [1]. This work was comprehensive and included all the major areas of chromatography. Specialist chapters covered the specific areas of size exclusion chromatography and ion-exchange